SYNTHESIS OF CARBON BASED FLUORESCENT NANOMATERIALS AND THEIR APPLICATIONS

THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF DEGREE

DOCTOR OF PHILOSOPHY

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I, ***"Subhash Chandra"***, certify that the work embodied in this thesis is my own bonafide work and carried out by me under the supervision of ***"Prof. Syed Hadi Hasan"*** from ***"July 2017" to "August 2022"***, at the ***"Department of Chemistry"***, Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not wilfully copied any other's work, paragraphs, text, data, results, *etc.*, reported in journals, books, magazines, reports dissertations, theses, *etc.*, or available at websites and have not included them in this thesis and have not cited as my own work.

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Dedicated to My Beloved
PARENTS

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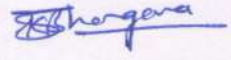

Subhash Chandra

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PA	Picric acid
TNT	Trinitro Toluene
c	Concentration absorbing molecule in $mol.m^{-3}$
FRET	Fluorescence resonance electron transfer
IFE	Inner filter effect
AuNPs	Gold nanoparticles
CIE	Commission Internationale de l'Éclairage
TRV	Toxicity Reference Value
LED	Light emitting diode
CNTs	Carbon nanotubes
LOAEL	Lowest observed adverse effect level
CQDs	Carbon quantum dots
N-CQDs	Nitrogen doped-CQDs
S-CQDs	Sulfur doped-CQDs
B-CQDs	Boron doped-CQDs
P-CQDs	Phosphorous doped-CQDs
NS-CQDs	Nitrogen sulfur co-doped CQDs
d	Interplanar spacing
HRP	Horseradish peroxidase
EDAX	Energy-dispersive X-ray spectroscopy
et al.	Co-authors
FT-IR	Fourier transform infrared spectroscopy
FL	Fluorescence
AA	Ascorbic acid
H_2O_2	Hydrogen peroxide
Phe	Phenol
NB	Nitrobenzene
2-CP	2–chlorophenol
2,4-DNP	2,4–dinitrophenol
Res	Resorcinol

IB	Iodobenzene
BB	Bromobenzene
1,3-DNB	1,3–dinitrobenzene
4-NP	4–nitrophenol
2-NP	2–nitrophenol
NaAc	Sodium acetate
I_0	Intensity of the incident radiation
RT	Room temperature
I_t	Intensity of the transmitted radiation
JCPDS	Joint committee on powder diffraction standards
LED's	Light emitting diodes
LOD	Limit of detection
RSD	Relative standard deviation
MRI	Magnetic resonance imaging
MTT	3-(4, 5-dimethylthiazol-2-yl)-2, 5-diphenyl-tetrazolium bromide
NaAc	Sodium acetate buffer
TSC	Thiasemicarbazide
oxTMB	Oxidized TMB
PBS	Phosphate buffer saline
XPS	X-ray photoelectron spectroscopy
TEM	Transmission Electron Microscopy
Km	Michaelis-Menton constant
Vmax	Maximum velocity
V	Initial velocity
QY	Quantum yield
QS	Quinine sulfate
$\mathbf{R^2}$	Correlation coefficient
SAED	Selected area diffraction pattern
t	Time (min)
IPA	Isopropyl alcohol

TPA	terephthalic acid
MA	Methyl alcohol
TiO_2	titanium oxide
CA	Citric acid
TMB	Tetramethylbenzidine
TA	Terephthalic acid
M-CQDs	Mustard carbon quantum dots
GO	Graphene oxide
XRD	X-ray diffraction spectroscopy
ε	Molar absorption coefficient
θ	Angle (degree)
λ	Wavelength
OPs	Organophosphates
Cpf	Chlorpyrifos
AChE	Acetylcholinesterase
ATCh	Acetylcholine
TCh	Thiocholine
TNBA	5-thio-2-nitrobenzoic acid
DTNB	5,5-dithiobis (2-nitrobenzoic acid)

Preface

This thesis describes the development of different kinds of carbon-based nanomaterials, which is synthesized from natural and organic carbon precursors for the detection of biosensors, pesticides and hazardous nitro compounds etc. These fluorescence small carbon nanoparticles have a particle size of less than 10 nm and are a promising nano-biotechnology material due to their smaller particle size, excellent biocompatibility, large surface and high surface energy, high quantum yield, excitation dependent photoluminescence behaviour, high water solubility, ease of production, and low toxicity. Due to their unique physicochemical, optical and electronic properties, these materials are a rising star in various fields such as biosensing, bioimaging, drug delivery, optoelectronics, photovoltaics, and photocatalysis. To improve their functionality and optical properties, CQDs have been synthesized from natural and chemical precursors using laser ablation, arc discharge, chemical oxidation, electrochemical oxidation, hydrothermal carbonization, and microwave irradiation. Among them are laser ablation and arc discharge, which require sophisticated and expensive equipment, as well as chemical oxidation and electrochemical oxidation, which require strong acids. While microwave irradiation provides an easy method for synthesizing CQDs within minutes, it is limited by its uncontrollable reaction conditions. It is common to choose the hydrothermal route currently due to its simplicity, rapidity, controlled reaction conditions, and cost-effectiveness. In addition, CQDs can also be synthesized using natural carbon sources due to their low cost, environmental friendliness, and widespread availability. There have been numerous studies using natural carbon sources, such as mustard seeds, soybeans, orange peel juice, green grass, milk, potatoes, plant leaves, soy milk, cocoon silk, and so forth, to synthesize CQDs. Various organic compounds have been

also used in the synthesis of CQDs, such as ascorbic acid, tartaric acid, citric acid, glycol, glucose, sucrose, and glycerol. Nevertheless, the primary challenge remains to develop CQDs that produce high quantum yields (QY).

Chapter 1 cover the basics of nanotechnology, its origins in brief, and the different types of nanomaterials. In addition to this, the section also contains a brief history of previous and ongoing research on the synthesis of CQDs and their applications. The goals and scope of the present investigation have been outlined at the end of this chapter.

Chapter 2 In this section, the experimental details, including the materials and instruments that have been used to fully characterize the carbon quantum dots, are discussed. In this chapter, the preparation of standard solutions and various calculations are also covered, such as quantum yields, quenching constants, and limit detection of detections.

Chapter 3 summarized the synthesis of fluorescent carbon quantum dots via facile one-step hydrothermal treatment of mustard seeds (M-CQDs). It showed excellent optical property with fluorescent quantum yield 4.6 %. The as-prepared M-CQDs exhibited peroxidase-like mimetic activity and catalyzed the oxidation of chromogenic substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H_2O_2 to produce a blue color reaction mixture with the prominent peak at 652 nm. Furthermore, the peroxidase-like activity performance of M-CQDs followed the steady-state kinetics behavior and exhibited similar catalytic activity as that of natural enzyme Horseradish peroxidase (HRP). In addition to this, the double reciprocal plot showed a parallel line which suggested the occurrence of Ping-Pong

type of mechanism. The H_2O_2 dependent oxidation of TMB was helpful for the colorimetric detection of H_2O_2 in the linear range of 0.02 to 0.20 mM with the limit of detection (LOD) of 0.015 mM. Interestingly, the oxidized TMB was further reduced to native TMB by the reducing agent ascorbic acid. Hence M-CQDs showed its potential towards the selective and sensitive detection of ascorbic acid in the linear range of 10 to 70 μM having a correlation coefficient of 0.998 with LOD of 3.26 μM. The practical feasibility of the proposed detection method of AA was also investigated in common fresh fruits.

Chapter 4 the present study aims the development of hazardous explosive picric acid sensor based on the NS-CQDs. In this work, we utilize a one-pot hydrothermal technique for the synthesis of nitrogen/sulfur-co-doped fluorescent carbon quantum dots (NS-CQDs) from citric acid (CA) and thiosemicarbazide (TSC). The obtained NS-CQDs exhibited strong blue emission under UV light, with fluorescence quantum yield (QY) of ~37.8%. The Commission internationale de l'eclairage (CIE) coordinates originated at (0.15, 0.07), which confirmed the blue fluorescence of the synthesized NS-CQDs. Interestingly, the prepared NS-CQDs were successfully used as a selective nanoprobe for the monitoring of environmentally hazardous explosive picric acid (PA) in different nitro- and non-nitro-aromatic derivatives of PA. The mechanism of the NS-CQDs was also explored, and was posited to occur via the fluorescence resonance electron transfer (FRET) process and non-fluorescent complex formation. Importantly, this system possesses excellent biocompatibility and low cytotoxicity in HeLa cervical cancer cells; hence, it can potentially be used for PA detection in analytical, environmental, and pathological applications. Furthermore, the practical applicability of the proposed

sensing system to pond water demonstrated the feasibility of our system along with good recovery.

Chapter 5 reports the green synthetic method for the synthesis of water-soluble fluorescent CQDs. Now a days, green route are significantly favoured for the synthesis of CQDs, which develop the use of natural renewable carbon sources. The use of green sources has several advantages due to zero cost, non-toxicity, environmental friendliness, and easy availability. In this study, we have synthesized fluorescent carbon quantum dots (J-CQDs) from Jatropha fruit by using a one-pot hydrothermal approach, for the first time. The as-synthesized J-CQDs exhibited bright blue fluorescence emission with a high quantum yield of 13.7 %. Furthermore, the synthesized fluorescent J-CQDs have been used as a fluorometric sensor for the detection of pesticides. The sensing of pesticides is based on the irreversible catalytic inhibition of acetylcholinesterase (AChE) enzyme with a controlled fluorescence quenching process. The thiocholine was mainly triggered by the decomposition of DTNB to form yellow-colored TNBA. Further, TNBA gradually quenched the fluorescence emission spectra of added J-CQDs via electron transfer process. The catalytic activity of AChE was inhibited in the presence of OPs, leading to the recovery of the fluorescence signal. Thus, a sensitive and selective nanoprobe was designed for the sensing of OPs (chlorpyrifos) along with a detection limit 2.7 ng/mL. Apart from this, the proposed sensing method has been successfully applied for pesticide detection in environmental and agricultural samples with acceptable recovery. Thus, the delivered result suggests that our probe is simple in design, having a short reaction time, and could be proficiently used in further analytical and environmental applications in the future.